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ELECTROCHEMICAL BEHAVIOR OF THE BORON ANODE IN AQUEOUS SOLUTIONS

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16. Abstract <p>The electrochemical oxidation of p-type boron in 0.2 N NaNO_3 solutions of pH 0.4 to 13.1 was studied by galvanostatic techniques. The capacitance of the electrode, Tafel slopes, and a limited analysis of reaction mechanism are reported. The anodic dissolution in acid solution is a charge-transfer-limited one-electron reaction to form a monovalent species in the overpotential region of 0.25 to 0.70 V. The dissolution in basic solution is most probably a one-electron charge-transfer reaction from a monovalent to divalent species involving three hydroxyl ions. Open circuit potentials were mixed potentials, probably due to hydrogen formation at open circuit but not contributing to the electrochemical reaction at the applied overpotential. Exchange currents, estimated by extrapolation of the Tafel line to the standard oxidation potential for the boron reaction, were of the order of 10^{-6} A/cm² in acid solution and 10^{-12} A/cm² in basic solution. The reaction order of the rate determining acidic and basic reactions was determined with regard to $[\text{H}^+]$ and $[\text{OH}^-]$. The level of illumination had no effect on the electrochemical behavior of the electrode.</p>					
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ELECTROCHEMICAL BEHAVIOR OF THE BORON ANODE IN AQUEOUS SOLUTIONS

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SUMMARY

The electrochemical oxidation of p-type boron in 0.2 N NaNO_3 solutions of pH 0.4 to 13.1 at room temperature was studied by galvanostatic techniques.

The capacitances of the electrodes were found to be normal, 10.5 microfarads per square centimeter in acid solutions and 25.9 microfarads per square centimeter in basic electrolyte.

Tafel plots were constructed and the slopes obtained were used to determine the charge-transfer rate determining reaction over the whole pH range. The rate determining reaction in acidic solution was found to be a one-electron transfer, $\text{B} \rightarrow \text{B}^+ + \text{e}^-$. The reaction $\text{B}^+ \rightarrow \text{B}^{++} + \text{e}^-$ was found to be the most probable rate determining step in basic solutions. In acid solutions, the reaction order with respect to hydrogen ion concentration was found to be zero. Analysis of transition time data at low hydroxide concentrations suggests that the rate determining step in basic solutions involves three hydroxyl ions: $\text{B}^+ + 3\text{OH}^- \rightarrow \text{B}(\text{OH})_3^- + \text{e}^-$. A value of 1.5×10^{-6} square centimeter per second was obtained for the diffusion coefficient of OH^- ion in 0.2 N NaNO_3 .

Open circuit potentials did not agree with thermodynamically calculated values. The discrepancy was attributed to mixed potentials, probably due to hydrogen formation at the open circuit potential. Hydrogen formation did not contribute appreciably to the overall reaction at the applied overpotentials.

Exchange currents were estimated by extrapolation of the Tafel data to the standard equilibrium potential for the boron oxidation reaction. The estimated currents were of the order of 10^{-6} ampere per square centimeter in acid solution and 10^{-12} ampere per square centimeter in basic solution.

The level of illumination had no effect on the electrochemical behavior of the electrode.

INTRODUCTION

The high theoretical half-cell potential of boron makes it an interesting candidate for, as Fleischer (ref. 1) has pointed out, an anode in primary batteries. Boron is a lightweight, trivalent material second only to beryllium in both gravimetric and volumetric energy density. It is unreactive with most acids, alkalis, and organic solvents (ref. 2). Possible oxide film formation, semiconductor behavior, and high resistivity may be involved in its electrochemical performance.

The electrochemical properties of boron have received very little attention. Chen and Salomen (ref. 3) measured the anodic efficiency of boron anodes in 0.1 N LiOH solution at 30° C. Individual measurements varied from 84.0 to 121 percent current efficiency with an average of about 98 percent efficiency.

In this study, constant current steps were applied anodically to boron electrodes in a 0.2 N NaNO₃ solution at room temperature varying in pH from 0.4 to 13.1. Measurement of the resultant potentials permitted the determination of the Tafel slope, the capacitance of the electrode, and a limited analysis of the mechanism of the reaction. The influence of the level of illumination on the electrochemical behavior was also investigated to determine if the boron electrode exhibits semiconductor properties.

EXPERIMENTAL

Electrode

Boron filaments 0.01016 centimeter (4 mils) in diameter deposited on a 0.00127-centimeter (0.5-mil) core of tungsten were used as the electrode material in this study. This material was supplied by a commercial source and was prepared by the method described in reference 4. Metallographs of a cross section of the filament indicated a homogeneous outer layer, presumably boron, with a second phase as a core. X-ray diffraction patterns obtained with both copper and chromium radiation showed the existence of WB₄ and W₂B₅ and no metallic tungsten in the core. No other compounds were present. Similar results are described by Warner and Satterfield (ref. 4), who published metallographic cross sections similar in appearance to those obtained in the present work. They also found evidence for a core composed solely of WB₄ and W₂B₅. They note that this composition results from vapor deposition of boron from a halide system.

Further evidence for the WB₄, W₂B₅-core was obtained by measuring the resistance of a given length of filament. The average resistivity was much larger than the value given by Touloukian (ref. 5) for tungsten ($5.2 \times 10^{-6} \Omega\text{-cm}$) and it corresponded almost exactly to that given for a tungsten boride compound (not WB₄ or W₂B₅, however) of 55×10^{-6} ohm-centimeter.

Lipsitt (ref. 6) used electron diffraction techniques to study the nature of the filament surface and concluded that the boron is a heavily faulted multilayered crystalline structure which is stable at temperatures up to 1000°C over an extended period of time.

The thermoelectric probe technique (ref. 7) indicated that the filaments used in this work were p-type semiconductors. The filaments were mounted for electrochemical study to a copper conductor by tungsten inert gas welding in an argon atmosphere. The bottom end was sealed with a transparent silicon rubber adhesive/sealant to prevent exposure of the core to the electrolyte.

All current densities are based on the measured geometrical area of the electrode (typically, 0.06 cm^2). Metallographic studies of the filaments following electrolysis showed the removal of boron to be regular with no cracking or pitting at magnifications of up to $\times 500$.

Electrochemical Cell

The cell used is shown in figure 1. It consists of a Pyrex vessel containing a platinum cup, which serves as the counter electrode. All potentials were measured relative to a commercial saturated calomel reference electrode with an asbestos thread junction encased in a glass envelope with a Luggin capillary. The working and reference electrodes were positioned in the center of the platinum cup. A Teflon magnetic stirrer was placed in the cell.

The electrolyte was 0.2 N NaNO_3 prepared from reagent grade NaNO_3 and distilled water, and the pH was adjusted over the range from 0.5 to 13.1 as desired by the addi-

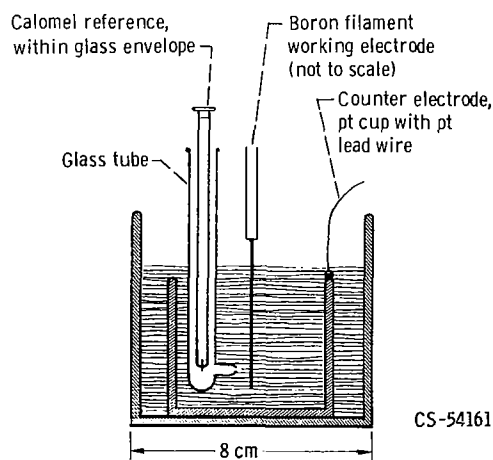


Figure 1. - Electrochemical cell.

tion of reagent grade HCl or KOH. The volume of electrolyte in the cell was approximately 200 cubic centimeters.

Instrumentation

Constant current steps adjusted to provide current densities in the range from 0.3 to 10 milliamperes per square centimeter were supplied to the electrode by means of a 1 to 3 microsecond rise time potentiostat and a conventional relay-pulse generator, which are shown schematically in figure 2. The resultant potential as a function of time

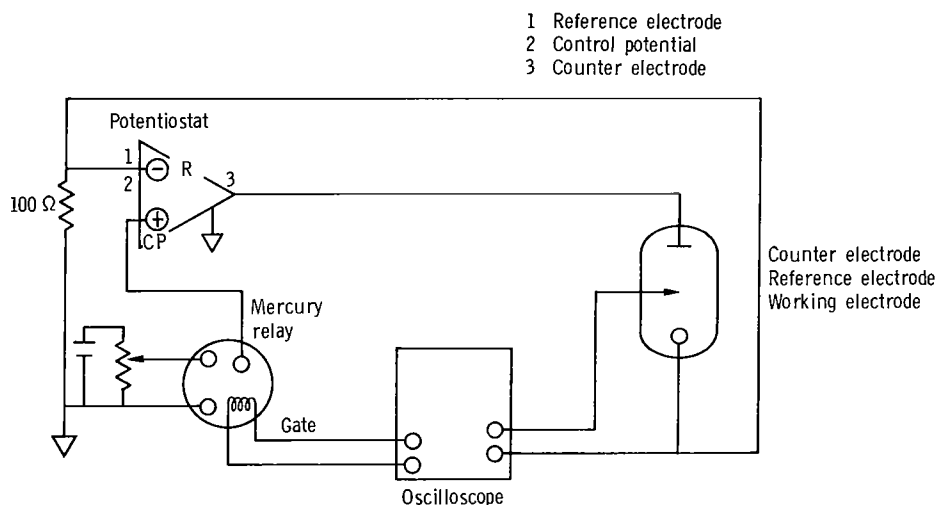


Figure 2. - Block diagram of circuit for galvanostatic measurements.

was displayed on an oscilloscope with a differential amplifier having an input impedance of 1 megohm paralleled by 4.7 picofarads. Photographs were taken of the traces during the first 350 microseconds following initiation of the pulse to permit calculation of the IR drop in the electrode and in the solution between the electrode surface and the tip of the Luggin capillary by observation of the initial potential jump. In addition, the differential double layer capacitance was obtained from the slope of the initial linear potential rise $(\partial\eta/\partial t)_{t \rightarrow 0}$ (fig. 3(a)) from the equation

$$C = \frac{i}{(\partial\eta/\partial t)_{t \rightarrow 0}}$$

where i is applied current density.

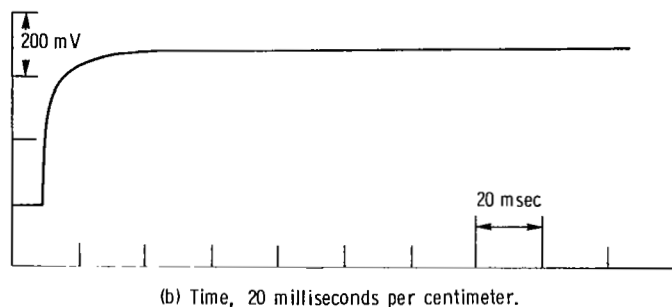
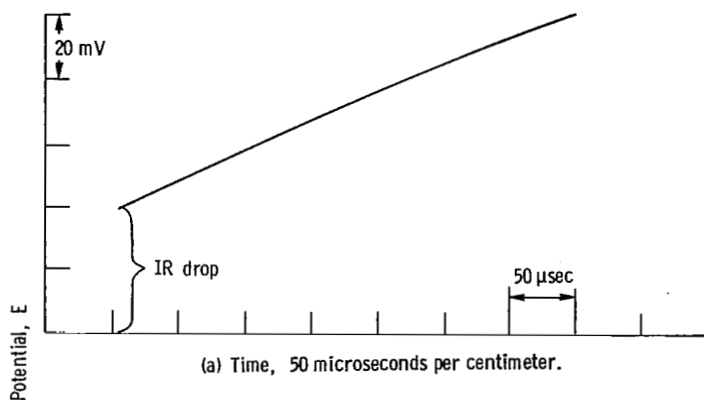


Figure 3. - Short and long time photographs of potential-time curves for boron anode at current density of 2.6 milliamperes per square centimeter.

Photographs taken over the time interval of 0 to 140 milliseconds permitted observation of the steady resultant potential. Figure 3(b) is typical of these photographs. In all cases, a steady potential was established within 80 milliseconds.

The influence of illumination was investigated in the 0.5 N HCl electrolyte using a 500-watt incandescent photoflood 1-foot from the electrode in room light and darkness. No differences in the electrochemical behavior were noted. Normal Tafel behavior and the absence of a photoeffect is expected for anodic dissolution reactions of p-type semiconductors by analogy with germanium (ref. 8).

Open circuit potentials were measured relative to the saturated calomel reference with a high input impedance ($>5000\text{ M}\Omega$) digital voltmeter. About 1 hour was required to reach a steady-state potential. Potentials were measured in the presence and absence of oxygen by bubbling either air or pure argon through the solution.

Analysis of Data

Potentials, assumed to be activation overpotentials, read from the photographs at 120 microseconds for various current density pulses were corrected for the IR drop and

plotted against the \log of the current density to give a Tafel plot. A straight line is indicative of a charge transfer rate determining step and the extrapolation of the straight line portion to the true $\eta = 0$ axis (equilibrium potential) gives the exchange current (i_0) for the reaction. The slope of the line $\partial \log i / \partial \eta$ may be used to calculate an apparent anodic charge transfer coefficient α , providing the charge transfer valence Z is known (ref. 9):

$$\alpha = \frac{(2.303) \left(\frac{\partial \log i}{\partial \eta} \right) RT}{ZF}$$

where

i applied current density, mA/cm², + anodic, - cathodic

η observed overpotential, mV, + anodic, - cathodic

Z charge transfer valence

F Faraday

R gas constant, 8.314 (V)(C)/mole deg

T temperature, K

RESULTS AND DISCUSSION

Electrode Potentials

Table I lists open circuit potentials for 0.05, 0.25, and 0.40 M H₃BO₃ solutions with 0.20 N NaNO₃ and either 0.05 N HCl or 0.02 N KOH. All potentials are reported relative to the standard hydrogen electrode. Identical potentials were obtained in an argon atmosphere and in air. The calculated values given in table I are obtained from the Nernst relation and Latimer's (ref. 10) standard equilibrium potentials and ionization constants for the following:

(1) Boron in acid solution: $3H_2O + B \rightarrow H_3BO_3 + 3H^+ + 3e^-$, $E^0 = -0.87$ volt

(2) Boron in basic solution: $B + 4OH^- \rightarrow H_2BO_3^- + H_2O + 3e^-$, $E^0 = -1.79$ volts

The experimental potentials are much less anodic than the calculated values, indicating the possibility of reactions other than those assumed in the calculation of E^0 or a mixed potential due to additional reactions such as hydrogen formation. The second explanation appears most likely and will be discussed in detail in the section Mixed Potentials.

TABLE I. - OPEN CIRCUIT POTENTIALS
FOR BORON (RELATIVE TO STANDARD
HYDROGEN ELECTRODE)

IN 0.20 N NaNO_3

Concentration of H_3BO_3 , moles/cm ³	Observed potential, V	Calculated potential, V
Acid solution, 0.05 N HCl		
0.05	+0.008 ± 0.011	-1.08
.25	-.001 ± .033	-1.06
.40	+.028 ± .006	-1.06
Basic solution, 0.02 N KOH		
0.05	+0.344	-1.68
.25	+.281	-1.67
.40	+.198	-1.66

Capacitance

The average differential capacitances of the electrode were 10.5 ± 1 and 25.9 ± 2 microfarads per square centimeter in acid and basic solutions, respectively. Capacitance values of this magnitude would indicate little if any oxide film formation in either pH range.

Tafel Behavior

Straight lines were obtained in Tafel plots of all the data, indicating the existence of a charge-transfer rate determining process. Figure 4 for 1 N HCl electrolyte is typical, where the linear region extends from about 0.25 to about 0.70 volt. No limiting currents were observed. Tafel slopes are summarized in table II for the electrolyte studies.

Mixed Potentials

A mixed potential between boron oxidation and hydrogen reduction reactions would (1) explain the near zero open circuit potential observed for acidic solutions, (2) allow

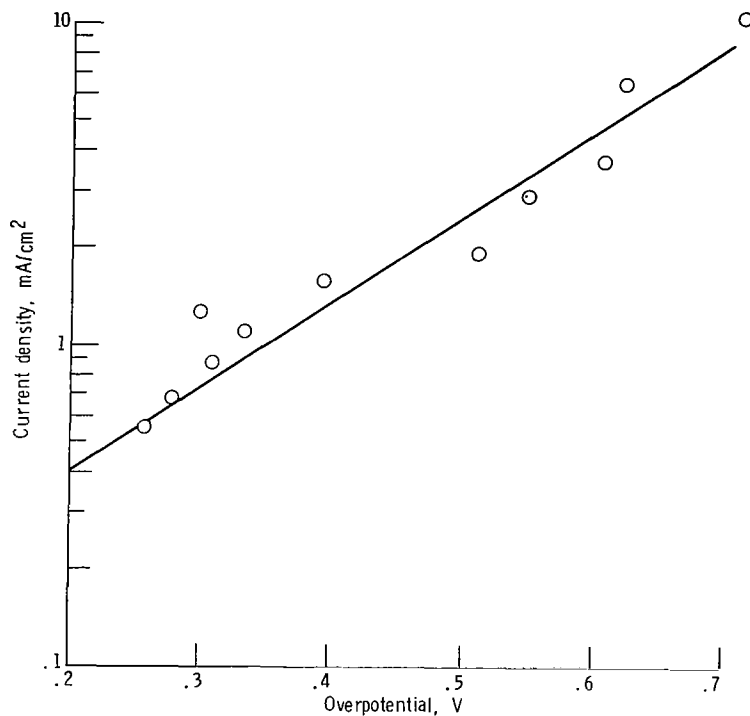


Figure 4. - Tafel plot for boron anode in acid solution (pH = 0.4; 1N HCl + 0.2 N NaNO₃).

TABLE II. - TAFEL SLOPES, OPEN CIRCUIT POTENTIALS, AND ESTIMATED EXCHANGE CURRENTS FOR BORON ANODES IN ACIDIC AND BASIC SOLUTIONS

Electrolyte	pH	Open circuit potential, relative to standard hydrogen electrode, V	Exchange current, A/cm ²	Tafel slope, ^a b _a
0.2 N NaNO ₃ + 1 N HCl	0.4	-0.009±0.019	2.3(±0.30)×10 ⁻⁶	2.303 RT/(0.052±0.003)(3F) = 0.379
.2 N NaNO ₃ + .05 N HCl	1.70	+.132±.006	.86(±.40)×10 ⁻⁶	2.303 RT/(0.068±0.003)(3F) = 0.290
.2 N NaNO ₃ + .002 N HCl	2.70	+.158±.046	.17(±.10)×10 ⁻⁶	2.303 RT/(0.087±0.003)(3F) = 0.227
.2 N NaNO ₃	5.45	+.228±.005	.17(±.10)×10 ⁻⁶	2.303 RT/(0.084±0.005)(3F) = 0.235
.2 N NaNO ₃ + .05 N KOH	11.9	+.594±.012	<10 ⁻¹²	2.303 RT/(0.603±0.03)(3F) = 0.0313
.2 N NaNO ₃ + 1 N KOH	13.1	+.671±.008	<10 ⁻¹²	2.303 RT/(0.435±0.03)(3F) = 0.0453

^aTafel slopes computer fit by least squares method. Errors listed are standard deviations.

for pure charge-transfer rate limited oxidation of boron in the anodic overpotential region of 0.25 to 0.70 volt, and (3) explain the observed evolution of hydrogen with the application of cathodic currents.

If the open circuit potential is a mixed potential, dissolution of boron into the electrolyte should occur with time. Electrolytes in which boron anodes were allowed to stand for 300 hours contained no detectable amounts of boron. Calculation shows, however, that corrosion currents as high as 0.7 milliamperes per square centimeter would produce boron concentrations of 8.5 ppm in the 200-milliliter electrolyte volume - a concentration just below the limit of detection of boron by chemical or atomic absorption techniques.

A mixed potential prevents extrapolation of the Tafel line to zero applied potential (the equilibrium potential for the oxidation reaction if no competing reactions are taking place) in order to determine the exchange currents. Since the equilibrium potential for the boron oxidation reaction was unknown, the exchange currents were approximated by extrapolating the Tafel line to the calculated standard equilibrium potential given in Latimer (ref. 10).

Table II contains exchange currents approximated in this way. In acidic solutions, both exchange currents and Tafel slope decrease as the pH approaches neutrality, an effect which is not understood. In basic solutions, the exchange currents are very small, less than 10^{-12} ampere per square centimeter, and the Tafel slope values are 0.033 and 0.045. Data on 0.001 N and 0.002 N KOH electrolytes are discussed later.

Reaction Order

The reaction order of the rate determining acidic reaction was studied by plotting current at a constant potential as a function of $[H^+]$. The acidic reaction current was found to be invariant with pH as seen in figure 5,

$$\frac{\partial \log i_a}{\partial \log [H^+]} = 0 \pm 0.03 = Z_{r, H^+}$$

where Z_{r, H^+} is the reaction order for H^+ on the left side of the reaction written for the anodic process (see Vetter, ref. 9, p. 435). This is in keeping with the overall reaction of $B + 3H_2O \rightarrow H_3BO_3 + 3e^- + 3H^+$ proposed by Latimer (ref. 10). The Tafel data for basic solutions were inadequate to determine the reaction orders.

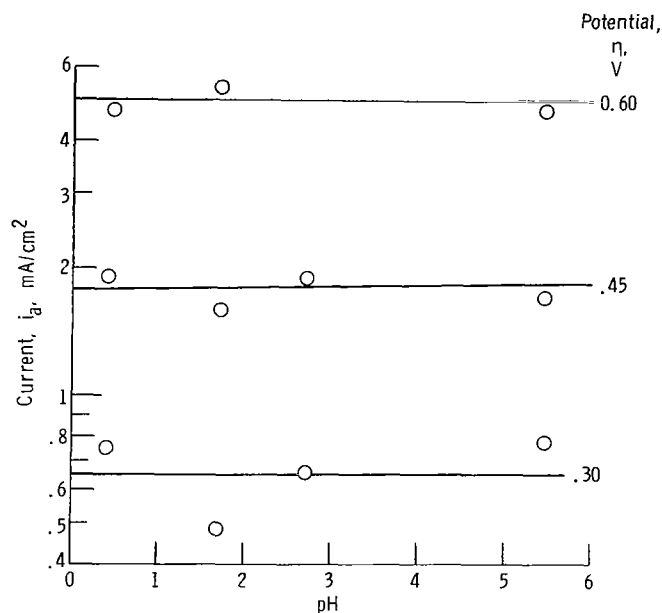
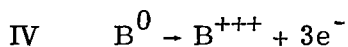
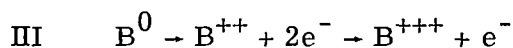
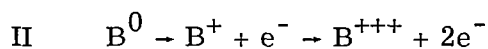
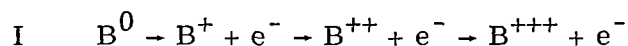


Figure 5. - Current as function of $[H^+]$ at fixed potentials for boron anode in acidic solution.

Reaction Mechanism

The Fraser and Barrados (ref. 11) method of quasi-equilibrium analysis of possible rate determining reactions was used to calculate Tafel slopes. The following consecutive anodic reactions were considered:

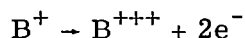
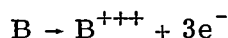
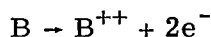


The calculated Tafel slopes in terms of the true anodic transfer coefficient β appear in table III. Comparison of these values with the measured slopes of table II indicates that the most probable rate determining step for acid solutions is $B \rightarrow B^+ + e^-$ with $\beta \cong 0.22$. For basic solutions it is $B^+ \rightarrow B^{++} + e^-$ with $\beta \cong 0.56$. Three other reactions in basic solution give reasonable values of β between 0.2 and 1.0, but all involve two electrons

TABLE III. - CALCULATED TAFEL SLOPES

Reaction mechanism	Rate determining step	Anodic Tafel slope, b_a
I, II	$B \rightarrow B^+ + e^-$	$2.303 RT/\beta F$
I	$B^+ \rightarrow B^{++} + e^-$	$2.303 RT/(\beta + 1)F$
I, III	$B^{++} \rightarrow B^{+++} + e^-$	$2.303 RT/(\beta + 2)F$
III	$B \rightarrow B^{++} + 2e^-$	$2.303 RT/(2\beta)F$
IV	$B \rightarrow B^{+++} + 3e^-$	$2.303 RT/(3\beta)F$
IV	$B^+ \rightarrow B^{+++} + 2e^-$	$2.303 RT/(2\beta + 1)F$

and are therefore less probable because of the high activation energy required to multi-electron transfers (ref. 12). They are



In addition to the Tafel results appearing in table II, data were also obtained using the slightly basic sodium nitrate electrolytes containing 0.001 N KOH and 0.002 N KOH. A transition time τ was observed in the potential traces obtained for these two electrolytes when current densities were less than 5 milliamperes per square centimeter. The inset of figure 6 is typical of such traces. The transition time is, of course, dependent on the current density applied. This is not due to electrolytic removal of a surface layer since the total charge involved $q = i\tau$ is not constant. However, the product $i(\tau)^{1/2}$, summarized in table IV, is independent of current density with average values of 0.31 and 0.63 for the 0.001 N and 0.002 N KOH solutions, respectively. The constancy of the $i(\tau)^{1/2}$ product indicates a diffusion controlled electrode process (ref. 13). The observation of this effect only at low KOH concentrations, the proportionality of $i(\tau)^{1/2}$ to the KOH concentration, and the consumption of OH^- in the overall reaction suggest that OH^- is the diffusing species. Through the use of the Sand equation (ref. 13) a reasonable value of 1.5×10^{-6} square centimeter per second is obtained for the diffusion coefficient.

Again referring to the inset in figure 6, the potential plateau prior to the transiting time τ gives Tafel slopes similar to those obtained from the more basic 0.05 N KOH

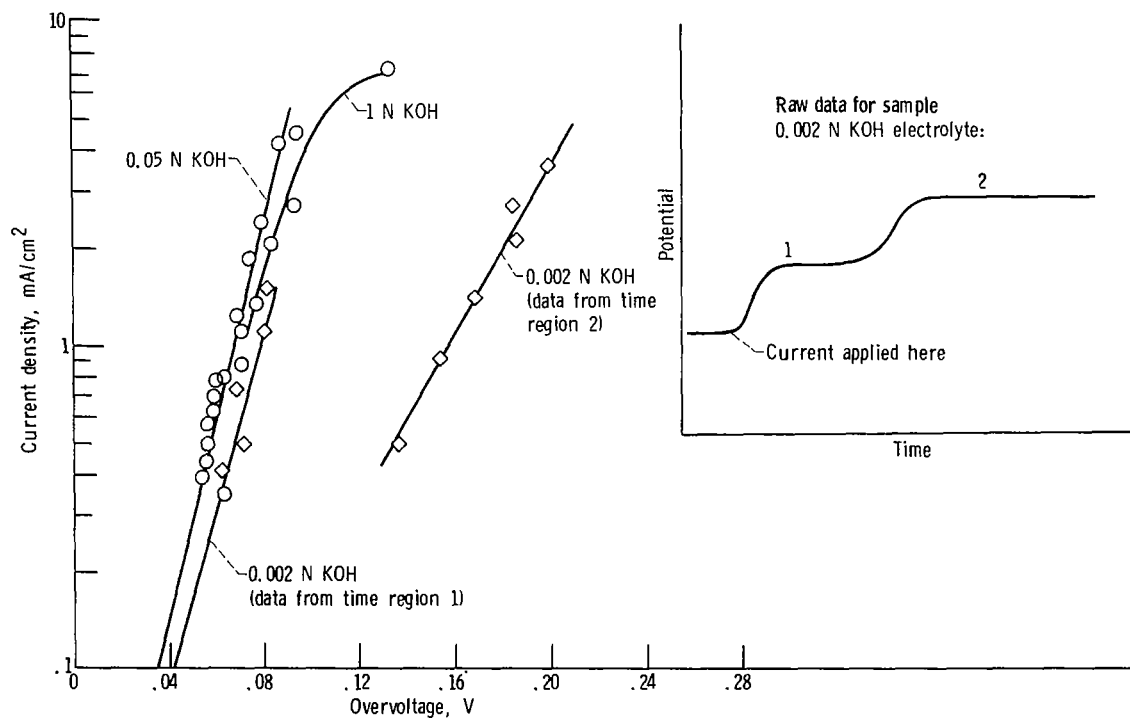


Figure 6. - Correspondence of Tafel slopes for 0.05 N KOH and 1 N KOH electrolyte and time region 1 of 0.002 N KOH electrolyte for 0.2 N NaNO₃ solutions.

TABLE IV. - $i(\tau)^{1/2}$ AT
VARIOUS CURRENT
DENSITIES

(a) 0.002 N KOH

Current density, i , mA/cm ²	$i(\tau)^{1/2}$ mA(sec) ^{1/2} /cm ²
0.790	0.70
1.13	.77
1.39	.67
2.10	.51
2.40	.63
2.73	.60
Average 0.63 ± 0.05	

(b) 0.001 N KOH

Current density, i , mA/cm ²	$i(\tau)^{1/2}$ mA(sec) ^{1/2} /cm ²
0.50	0.33
.645	.32
.790	.19
.905	.31
1.13	.38
Average 0.31 ± 0.05	

TABLE V. - TAFEL SLOPES - BORON ANODES IN
0.001 N KOH AND 0.002 N KOH ELECTROLYTE

Electrolyte	pH	Time period	Tafel slope
0.2 N NaNO ₃ + 0.001 N KOH	10.3	1	2.303 RT/(0.576±0.06)(3)(F)
		2	2.303 RT/(0.255±0.03)(3)(F)
0.2 N NaNO ₃ + 0.002 N KOH	10.7	1	2.303 RT/(0.540±0.05)(3)(F)
		2	2.303 RT/(0.291±0.04)(3)(F)

and 1 N KOH electrolytes. Table V summarizes data from this plateau (time period 1) and data from the constant potential following τ (time period 2). The data from time period 2 also give a linear Tafel plot (fig. 6) but must represent a mixed reaction including some diffusion of OH⁻ to the surface. The Tafel slopes here are intermediate between the slopes for the acid and the basic electrolytes.

For the dilute KOH solutions, the overpotential-time behavior in time period 1 is characterized by a charge-transfer limited reaction becoming partially diffusion controlled. Since the electrode is heavily polarized relative to the equilibrium potential ($\eta \gg RT/nF$), the equation derived and discussed by Vetter (ref. 9, p. 357) can be used to advantage. A plot of the function $\log(1 - \sqrt{t/\tau})$ against η should be a straight line for the case where a species like OH⁻ is being depleted by electrochemical reaction. Typical examples of these plots are shown in figure 7. The slope is equal to $(-1/b_a z_{r, OH^-})$ where b_a is the Tafel slope (see table IV) and z_{r, OH^-} is the reaction order with respect to OH⁻. A value of $z_{r, OH^-} = 3.1$ is obtained. This implies that three OH⁻ ions

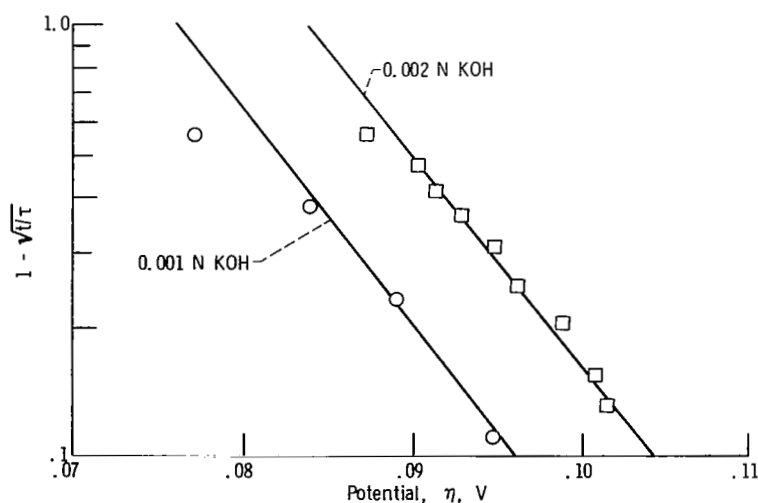
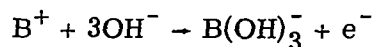
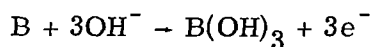
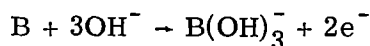


Figure 7. - Plot of $1 - \sqrt{t/\tau}$ as function of potential.

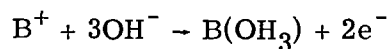
are involved in the rate determining charge-transfer step. That is, for the one-electron transfer



one cannot unambiguously rule out the possibility of a multielectron rate determining step on the basis of the Tafel data. Hence, reactions



or



could also be invoked in basic solution though they are less likely for reasons already mentioned.

Transition times were not observed for 0.05 N KOH and 1 N KOH solutions. In these cases, the concentrations of OH^- are so great that large current densities and long electrolysis times would be required to deplete the OH^- near the electrode. The largest current density used, 4.5 milliamperes per square centimeter, would have a transition time of 40 seconds in a 0.05 N KOH electrolyte. The current step actually lasted only about 0.2 second.

CONCLUSIONS

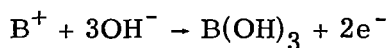
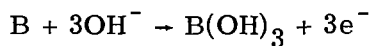
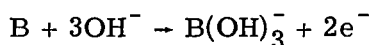
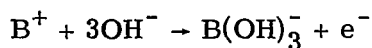
The p-type boron appears to undergo uniform dissolution in 0.2 N NaNO_3 electrolytes over a range of pH from 0.4 to 13.1 without pitting or cracking. The major component of the resistance of the electrode appears to be due to the tungsten boride core, so that the conductance could conceivably be improved by the deposition of boron on a more suitable electronic conductor. No variation in the current-voltage behavior with illumination was noted.

Neither acid nor basic electrolyte systems achieved the thermodynamic equilibrium potential, a situation attributed to a mixed potential arising from the hydrogen evolution reaction. Exchange currents were estimated by extrapolation of the Tafel data to the standard oxidation potential for the boron oxidation reaction. The magnitude of the ex-

change currents was of the order of 10^{-6} ampere per square centimeter for acid solution and 10^{-12} ampere per square centimeter for basic solutions.

The capacitance of the electrode is normal. Values of 10.5 microfarads per square centimeter and 25.9 microfarads per square centimeter were obtained for acidic and basic solutions, respectively.

In the anodic overpotential region of 0.25 to 0.75 volt, the reaction appears to be charge-transfer limited in both acidic and basic solutions. The rate determining step in acidic solutions from consideration of Tafel slopes appears to be the one-electron transfer $B \rightarrow B^+ + e^-$. The rate determining step in basic solution is somewhat ambiguous. Consideration of Tafel slopes and the reaction order with respect to OH^- , determined chronopotentiometrically, leads to four possible rate determining reactions:



The one-electron transfer is most probable on energetic grounds.

The diffusion coefficient for OH^- in 0.2 N $NaNO_3$ solution was estimated to be 1.5×10^{-6} square centimeter per second from transition time determinations.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 24, 1971,
113-34.

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